

*Citation:*

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tuting the other  $H$ -atoms by feeble morphotropic groups such as  $\text{NO}_2$ .

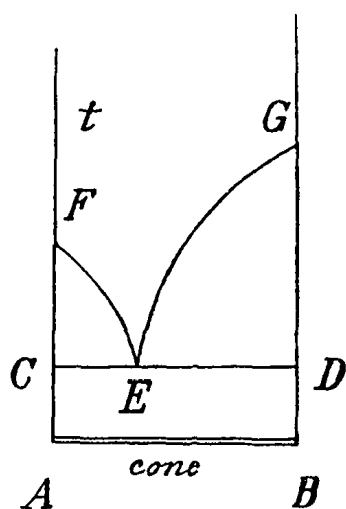
In regard to this, he recently informed me that both form a dinitroderivative, but with a different melting point and that not only the isomorphism is completely preserved, but that even the typical twin formation in certain solvents takes place with both in exactly the same manner, so that it looks as if one were dealing with the same material.

**Chemistry.** — "*The sublimation lines of binary mixtures*". By Prof. H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of November 28, 1903).

From the consideration of the  $p, t, x$ -representation of the equilibria for solid, liquid and gaseous phases of binary mixtures given by me a short time ago <sup>1)</sup> it may be deduced in what manner the evaporation of the mixtures of two *solid* substances, or inversely their condensation on cooling a mixture of vapours, takes place at a constant pressure by a change of temperature.

It is only necessary to take a  $t, x$ -section at constant pressure through the figure at such a height, that no other equilibria occur than those between solid and vapour or between solid and solid. This is possible as long as we keep below the pressure of the quadruple-point where solid  $A$ , solid  $B$ , liquid and vapour coexist.



The adjoined figure then indicates the general character of the section, in which the vertical axis represents the temperature and the horizontal axis the concentrations of the mixtures.

$F$  is then the sublimation temperature of the pure substance  $A$ ,  $G$ , that of pure  $B$ . These temperatures are depressed along the lines  $FE$  and  $GE$  until, below the point  $E$ , total condensation of the vapour mixture to solid  $A +$  solid  $B$  occurs.

Conversely the sublimation commences at the temperature given by the line  $CED$  and one of the two solid substances then disappears according to the concentration, unless the composition corresponds with  $E$ , in which case they both sublime simultaneously.

<sup>1)</sup> These Proc. V, p. 279.

If one of them has remained, the further sublimation takes place at a constantly increasing temperature until the point of the line  $FE$  or  $GE$  is reached, which corresponds with the original concentration of the mixture.

The whole figure is quite analogous with that representing the solidification or fusion of binary mixtures in which only the two components occur as solid phases,  $FE$  and  $GE$  resemble the melting point lines,  $E$  the eutectic point.

The analogy also holds good for the initial parts of the sublimation lines, for whose direction a formula similar to that for the lowering of the melting point may be deduced.

For the equilibrium of a single solid substance with its vapour we have the relation

$$\frac{dlp}{dt} = \frac{Q}{2T^2}$$

which is true for the increase of the sublimation pressure, when  $Q$  represents the molecular heat of evaporation of the solid substance.

If we now assume that a small part of this line is straight and that  $Q$  is constant, then if the pressure  $p$  is diminished by  $\Delta p = 0.01 p$  the sublimation temperature will diminish by  $\Delta T$ , for which we find:

$$\Delta T \times \frac{Q}{2T^2} = \frac{\Delta p}{p} = 0.01$$

$$\Delta T = \frac{0.02 T^2}{Q}$$

If we now add to the vapour of the solid substance, which has at  $T - \Delta T$  a pressure  $p - 0.01 p$ , 1 mol. % of the vapour of a second substance, the total pressure again becomes  $p$  and  $T - \Delta T$  is therefore, at that pressure, the sublimation temperature of the solid substance with 1 mol. % of admixture. Consequently  $\Delta T$  is also the lowering of that sublimation temperature by 1 mol. % of admixture.

The formula for the decrease therefore corresponds perfectly with that for the molecular lowering of the freezing point, provided that we take for  $Q$  the molecular heat of sublimation.

The formula, however, only applies in the case of exceedingly small quantities of admixture, as the supposition that the  $p, t$ -line for the equilibrium of a single solid substance with its vapour is a straight one, is incorrect.

If we take into consideration its curvature, it follows that the sublimation lines of each solid substance of the mixture are concave to the  $x$ -axis.

The lower the sublimation temperature of the added substance, the further downward the course of the sublimation line of a solid substance will extend. If, therefore, gases are used as admixtures and in sufficient excess, any solid substance ought, theoretically, to volatilise at a very low temperature.

Of this circumstance advantage has often been taken in the artificial preparation of minerals by sublimation-methods in which gases or vapours ( $NH_4Cl$ ) have been used as second substance.

If, however, they exercise a chemical action on the others, the sublimation phenomena belong to systems of three or more components.

The sublimation phenomena may also be accompanied by phenomena of fusion, as may be deduced from an examination of other sections through my three dimensional figure.

**Chemistry.** — “*A quantitative research concerning BAEYER's Tension Theory.*” By Prof. A. F. HOLLEMAN and Dr. G. L. VOERMAN.

(Communicated in the meeting of November 28, 1903).

BAEYER's tension theory gives an explanation of numerous phenomena in organic chemistry, but it is, however, almost exclusively of a qualitative nature. The preference for the formation of cyclic compounds with 5 and the instability of cycle systems with a larger or smaller number of atoms required by the theory are confirmed in many instances. Meanwhile as far as I am aware, that “preference” and that “instability” has never been expressed in figures. And so long as this is not the case such expressions remain vague, as we do not possess any measure with which we can gauge the “preference” for the cycle formation with 5 over one with a different number of atoms, and also are not in a position to compare the stability of one compound with that of another.

I, therefore, suggested to Dr. VOERMAN to investigate quantitatively the relative stability of the members of a special class of cyclic systems, namely the anhydrides of the dibasic acids of the normal saturated series. They are again converted by the action of water into the dibasic acids. The ease with which they re-absorb water must depend on the degree of tension in the ring contained in these anhydrides, as the ring opens and the bonds then can retake their normal position. The velocity with which these anhydrides are converted into the corresponding acids may therefore, be taken as the measure of the tension in the ring.